Monsanto

MONSANTO CHEMICAL INTERMEDIATES CO.
Sauget, Illinois 62201
Phone: (618) 271-5835

2347-78

October 5, 1978

Illinois Environmental Protection Agency
Division of Water Pollution Control
Permit Section
2200 Churchill Road
Springfield, IL 62706

Dear Sir:

Please find attached, two copies of our application for a construction and operation permit for the Chlor-Alkali Phase II Rehabilitation project at our plant. This pre-treatment project will utilize the Akzo Imac TMR process to lower the mercury concentration from waste water before discharge from the Chlor-Alkali Department. Please note that this project will not increase the waste water flow rate.

Your approval of this joint Construction and Operating Permit is respectfully requested.

J. W. Molloy
Plant Manager

/tm
attachment

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ILLINOIS ENVIRONMENTAL PROTECTION AGENCY
DIVISION OF WATER POLLUTION CONTROL
PERMIT SECTION

Springfield, Illinois 62706

APPLICATION FOR PERMIT OR CONSTRUCTION APPROVAL

WPC-PS-1

1. NAME AND LOCATION:

Name of project: Chlor-Alkali Phase II Rehabilitation

Municipality or Township Village of Sauget County St. Clair

2. BRIEF DESCRIPTION OF PROJECT: Project will remove mercury from waste waters before discharge per proprietary technology purchased from AKZO.

3. DOCUMENTS BEING SUBMITTED: If the project involves any of the items listed below, submit the corresponding schedule, and check the appropriate spaces.

PROJECT

Private Sewer Connection....A	___	Spray Irrigation....H	___
Public Sewer Extension....B	___	Septic Tanks....I	___
Sewer Extension Construct Only....C	___	Industrial Treatment or Pretreatment....J	X
Sewage Treatment Works....D	___		
Excess Flow Treatment....E	___	Cyanide Acceptance....L	___
Lift Station/Force Main....F	___	Updating Cyanide Acceptance Form....M	___
Sludge Disposal....G	___	Waste Characteristics....N	X

Plans: Title Attachments 1 through 8

Number of Pages 24

Specifications: Title ______

Number of Books/Pages ______

Other Documents (Please Specify) ______

4. THIS IS AN APPLICATION FOR (CHECK):
 X A. Joint Construction And Operating Permit
 ___ B. Authorization To Construct (For Treatment Units Requiring NPDES Permits) NPDES Permit No. IL ______
 ___ C. Construct Only Permit (Does Not Include Operations)
 ___ D. Operate Only Permit (Does Not Include Construction) (Date of Issuance) ______

5. CERTIFICATIONS AND APPROVAL:

5.1 Certificate by ~~[illegible]~~ Engineer

I hereby certify that I am familiar with the information contained in this application and that to the best of my knowledge and belief such information is true, complete and accurate.

ENGINEER M. R. Foresman — NAME
IL 62-32267 — REGISTRATION NUMBER

FIRM Monsanto Co.

ADDRESS Rt. 3 Sauget, IL 62201

PHONE NUMBER (618) 271-5835

SIGNATURE Michael Ryan Foresman

WPC-150 Rev. 10/77

CERTIFICATIONS AND APPROVALS FOR PERMITS (USE ITEM 7 FOR AUTHORIZATION TO CONSTRUCT):

6.1 Certificate by Applicant(s)

I/We hereby certify that I/we have read and thoroughly understand the conditions and requirements of this Application.
I/We hereby agree to conform with the Standard Conditions and with any other Special Conditions made part of the Permit.

6.1.1 NAME OF APPLICANT FOR PERMIT TO CONSTRUCT Monsanto

STREET	CITY	STATE	ZIP CODE
Rt. 3	Sauget	IL	62201

SIGNATURE Jack W. Mellon DATE 10/5/

TITLE Plant Manager

6.1.2 NAME OF APPLICANT FOR PERMIT TO OWN AND OPERATE Monsanto

STREET	CITY	STATE	ZIP CODE
Rt. 3	Sauget	IL	62201

SIGNATURE Jack W. Mellon DATE 10/5/

TITLE Plant Manager

6.2 Attested (Units of Government)

DATE _____ SIGNATURE _____ TITLE _____ (CITY CLERK, VILLAGE CLERK, SANITARY DISTRICT CLERK, ET CETERA)

6.3 Applications from non-governmental applicants which are not signed by the owner, must be signed by a principal executive officer of at least the level of vice president, or his duly authorized representative.

6.4 Certificate by INTERMEDIATE SEWER OWNER *See attached addendum A

I hereby certify that the sewers to which this project will be tributary have adequate reserve capacity to transport the wastewater that will be added by this project without causing a violation of the Environmental Protection Act or Chapter 3 of the Regulations as adopted by the Illinois Pollution Control Board.

Name of sewer system to which this project will be tributary:

NAME OF SEWER SYSTEM OWNER _____

STREET CITY STATE ZIP CODE

SIGNATURE _____ DATE _____ TITLE _____

6.5 Certificate by Waste Treatment Works ~~Owner~~ Operator *See attached addendum A

I hereby certify that the treatment works to which this project will be tributary have adequate reserve capacity to treat the wastewater that will be added by this project without causing a violation of the Environmental Protection Act or Chapter 3 of the Regulations as adopted by the Illinois Pollution Control Board.

Name and location of waste treatment works to which this project will be tributary Sauget Waste Treatment Plant

TREATMENT WORKS OWNER Village of Sauget

STREET	CITY	STATE	ZIP CODE
	Sauget	IL	62201

SIGNATURE [illegible signature] DATE 10/5/78 TITLE Treasurer - Board of Trustees

7. CERTIFICATE BY APPLICANT FOR AUTHORIZATION TO CONSTRUCT (CONSTRUCTOR):

I hereby certify that I have read and thoroughly understand the requirements of this application and I am authorized to sign this application for authorization to construct in accordance with the Rules and Regulations of the Illinois Pollution Control Board.

SIGNATURE _____

PRINTED NAME OF PERSON SIGNING _____

TITLE _____

ORGANIZATION _____

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DIVISION OF WATER POLLUTION CONTROL
PERMIT SECTION
Springfield, Illinois 62706

SCHEDULE J INDUSTRIAL TREATMENT WORKS CONSTRUCTION OR PRETREATMENT WORKS

1. NAME AND LOCATION:

1.1 Name of project Chlor-Alkali Phase II Rehabilitation

1.2 Plant Location

1.2.1 Quarter Section ____ Section ____ Township Centreville Range ____ P.M. ____

1.2.2 Latitude 38° 35' 45" North

Longitude 90° 10' 49" West

1.2.3 Name of USGS Quadrangle Map (7.5 or 15 Minutes) Cahokia Quadrangle, IL/MO, 7.5 series

2. NARRATIVE DESCRIPTION AND SCHEMATIC WASTE FLOW DIAGRAM (see instructions)

The waste water stream from the existing sulfide treatment system will be further treated by a process purchased from AKZO Chemie Zout to solubilize and remove additional mercury. (See attachments 1 thru 8).

2.1 PRINCIPAL PRODUCTS: N/A

2.2 PRINCIPAL RAW MATERIALS: N/A

3. DESCRIPTION OF TREATMENT FACILITIES:

3.1 Submit a flow diagram through all treatment units showing size, volumes, detention times, organic loadings, surface settling rate, weir overflow rate, and other pertinent design data. Include hydraulic profiles and description of monitoring systems.

3.2 Waste Treatment Works is: Batch ____, Continuous X; No. of Batches/day ____, No. of Shifts/day ____

3.3 Submit plans and specifications for proposed construction.

3.4 Discharge is: Existing X; Will begin on ____.

4. DIRECT DISCHARGE IS TO: Receiving Stream ____ Municipal Sanitary Sewer X, Municipal storm or municipal combined sewer ____. If receiving stream or storm sewer indicated complete the following:

Name of receiving stream ____; tributary to ____;

tributary to ____; tributary to ____.

5. Is the treatment works subject to flooding? If so, what is the maximum flood elevation of record (in reference to the treatment works datum) and what provisions have been made to eliminate the flooding hazard? NO

6. APPROXIMATE TIME SCHEDULE: Estimated construction schedule:

Start of Construction December 1, 1978; Date of Completion December 1, 1979

Operation Schedule Continuous; Date Operation Begins December, 1979

100% design load to be reached by year 1980.

WPC-158

7. DESIGN LOADINGS

7.1 Design population equivalent (one population equivalent is 100 gallons of wastewater per day, containing 0.17 pounds of BOD_5 and 0.20 pounds of suspended solids; N/A

BOD______________; Suspended Solids______________; Flow______________.

7.2 Design Average Flow Rate______________MGD.

7.3 Design Maximum Flow Rate______________MGD.

7.4 Design Minimum Flow Rate______________MGD.

7.5 Minimum 7-day, 10-year low flow__________cfs__________MGD.

Minimum 7-day, 10-year flow obtained from______________.

7.6 Dilution Ratio_______;_______.

8. FLOW TO TREATMENT WORKS (if existing):

8.1 Flow (last 12 months)

8.1.1 Average Flow 0.13 MGD (90 GPM normal)

8.1.2 Maximum Flow 0.216 MGD (150 GPM Design)

8.2 Equipment used in determing above flows Two (2) - 400,000 gal. hold tanks.

9. Has a preliminary engineering report for this project been submitted to this Agency for Approval?

YES___ NO___. If so, when was it submitted and approved. Date Submitted______________

Certification#______________

Dated______________

10. List Permits previously issued for the facility:______________

11. Describe provisions for operation during contingencies such as power failures, flooding, peak loads, equipment failure, maintenances shut-downs and other emergencies.

Operations not required during such contingencies.

12. Complete and submit Schedule G if sludge disposal will be required by this facility.

13. WASTE CHARACTERISTICS: Schedule N must be submitted. liquid only

14. TREATMENT WORKS OPERATOR CERTIFICATION: List names and certification numbers of certified operators:

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ILLINOIS ENVIRONMENTAL PROTECTION AGENCY
DIVISION OF WATER POLLUTION CONTROL
PERMIT SECTION
Springfield, Illinois 62706

SCHEDULE N WASTE CHARACTERISTICS

1. Name of Project Chlor-Alkali Phase II Rehabilitation, Mercury Recovery

2. FLOW DATA

	EXISTING	PROPOSED-DESIGN
2.1 Average Flow (gpd)	130,000	130,000
2.2 Maximum Daily Flow (gpd)	216,000	216,000

2.3 TEMPERATURE

Time of year	Ave. Intake Temp. F	Avg. Effluent Temp. F	Max. Intake Temp. F	Max. Effluent Temp. F	Max. Temp. Outside Mixing Zone F
SUMMER	90	90			
WINTER	85	85			

2.4 Minimum 7-day, 10-year flow: N/A cfs ______ MGD.

2.5 Dilution Ratio: N/A ; ______

2.6 Stream flow rate at time of sampling ______ cfs .130-.216 MGD.

3. CHEMICAL CONSTITUENT Existing Permitted Conditions ___; Existing conditions ___; Proposed Permitted Conditions ______.

Type of sample: ___grab (time of collection___); X composite (Number of samples per day 1)

(see instructions for analyses required)

Constituent	RAW WASTE (mg/1)	TREATED EFFLUENT Avg. (mg/1)	TREATED EFFLUENT Max.	UPSTREAM SAMPLES (mg/1)	DOWNSTREAM SAMPLES (mg/1)
Ammonia Nitrogen (asN)	–	–			
Arsenic (total)	–	–			
Barium	–	–			
Boron	–	–			
BOD_5	–	–			
Cadmium	–	–			
Carbon Chloroform Extract	–	–			
Chloride	–	–			
Chromium (total hexavalent)	–	–			
Chromium (total tribalent)	–	–			
Copper	–	–			
Cyanide (total)	–	–			
Cyanide (readily released @150°F & pH 4.5)	–	–			
Dissolved Oxygen	–	–			
Fecal Coliform	–	–			

	RAW WASTE (mg/l)	TREATED EFFLUENT Avg. (mg/l) Max.	UPSTREAM (mg/l)	DOWNSTREAM SAMPLES (mg/l)
Fluoride	–	–		
Hardness (as $CaCO_3$)	–	–		
Iron (total)	–	–		
Lead	–	–		
Manganese	–	–		
MBAS	–	–		
Mercury	.020–.070	– .005	N/A	N/A
Nickel	–	–		
Nitrates (asN)	–	–		
Oil & Grease (hexane solubles or equivalents)	–	–		
Organic Nitrogen (as N)	–	–		
pH	6–8	6–8	N/A	N/A
Phenols	–	–		
Phosphorous (as P)	–	–		
Radioactivity	–	–		
Selenium	–	–		
Silver	–	–		
Sulfate	–	–		
Suspended Solids	–	–		
Total Dissolved Solids	–	–		
Zinc	–	–		
Others				

Addendum A

Construction and Operation of this pre-treatment process will not increase the amount of flow discharged to the Village of Sauget sewer system and Waste Water Trearment Plant.

ATTACHMENT 1

Reprinted from
Journal of Chromatography, 102 (1974) 443-450

CHROM. 7705

THE AKZO PROCESS FOR THE REMOVAL OF MERCURY FROM WASTE WATER*

G. J. DE JONG and C. J. N. REKERS
Akzo Zout Chemie Nederland B.V., P.O. Box 25, Hengelo (The Netherlands)

SUMMARY

Akzo Zout Chemie has developed a process for the removal of mercury from waste water, primarily in order to have a definite solution to the waste water problems of its own chlor-alkali plants. The Akzo process guarantees a very low concentration of mercury in the effluent even under strongly fluctuating conditions. The secondary pollution problems generated are extremely small compared with those in other processes. The mercury is efficiently recycled into the process. The process is competitive with other processes for the removal of mercury from waste water.

INTRODUCTION

The poisonous character of organic mercury compounds has been known for a long time. Organic mercurials have been used as fungicides, *e.g.*, for seed-dressing, and acute poisoning by organic mercurials occurred when contaminated corn seed was consumed.

Originally, inorganic mercury compounds were considered to be relatively harmless; calomel was once used as a laxative! This opinion changed when it was found that living organisms could transfer inorganic mercury into organically bound mercury, which penetrated the food chain algae → fish → man. The first case of poisoning of man by mercury from waste, due to the accumulation of mercurials in the food chain, was observed in Japan (Minimata disease).

This knowledge, when presented to industry, resulted immediately in greater efforts to decrease mercury losses to the environment. One of the main consumers of mercury is the chlor-alkali industry. Most of the mercury used in this industry ends up in waste streams, which are relatively well defined. Since 1970, the authorities have put strong pressure upon this branch of industry to reduce mercury losses. At that time, in most chlor-alkali plants, processes to reduce mercury losses, based on the favourable economics of the recovery of the expensive metal mercury, were already in operation, but further reduction of these losses required the introduction of a series of additional techniques.

* Also presented at the First International Mercury Congress, Barcelona, May 1974.

The protection of the environment against pollution is the main objective of these new techniques, and the value of regenerated mercury is no longer of importance with respect to the operational costs involved. For the evaluation of mercury pollution abatement processes, the following factors are considered to be important:

(a) the residual mercury concentration in the treated effluent;

(b) the secondary pollution problems generated by the processes under consideration;

(c) possibilities for recycling the recovered mercury;

(d) the relative cost of the various processes.

When trying to solve pollution problems in which pollutants of a persistant nature are involved, special attention should be paid to avoiding the concentration of a pollutant in a solution or solid that cannot be recycled.

SELECTION OF A PROCESS

Recognizing the fact that any method for solving a pollution problem generates a secondary problem, the following basic criteria for the selection of a suitable process for the removal of mercury from chlor-alkali waste water have been used at Akzo Zout Chemie:

(a) secondary pollution problems should be minimal;

(b) mercury should be recycled;

(c) the residual mercury concentration in the treated effluent should be low enough to meet the most stringent regulations expected;

(d) this residual mercury concentration should not be influenced by variations in the composition of the waste water, for chlor-alkali waste water concerns in particular the sodium chloride concentration.

Three basic possibilities for the removal of mercury from chlor-alkali plant waste water have been considered, *viz.*, precipitation as metallic mercury, precipitation as mercury(II) sulphide and ion exchange. Both of the precipitation processes have been discounted, mainly because of their secondary pollution problems. Fig. 1 shows the mercury flow in a precipitation process compared with that of an ion-exchange process.

In the precipitation process, mercury in the waste water is transferred to solid waste and, for the recovery of the mercury, this solid waste has to be treated. Dry distillation is commonly used for this purpose. During dry distillation, most of the mercury is transferred to the gas phase and a solid waste is obtained. The mercury-bearing gas is cooled, and both mercury and water vapour condense. The mercury phase and the water phase are separated, and the water is recycled to the start of the waste water process. The gas is still rich in mercury and is treated separately, *e.g.*, by iodised activated carbon. This carbon is then recycled to the solid waste treatment.

In an ion-exchange process, the mercury from the waste water is removed by an ion-exchange resin and, at the end of the cycle, the resin is regenerated and the regeneration liquid containing the mercury is returned to the process. The resin is re-used. A small amount of solids originally present in the waste water stream remains as solid waste, together with some spent resin. An ion-exchange process potentially meets the first two selection criteria (low secondary pollution and recycling of the mercury) better than the precipitation processes.

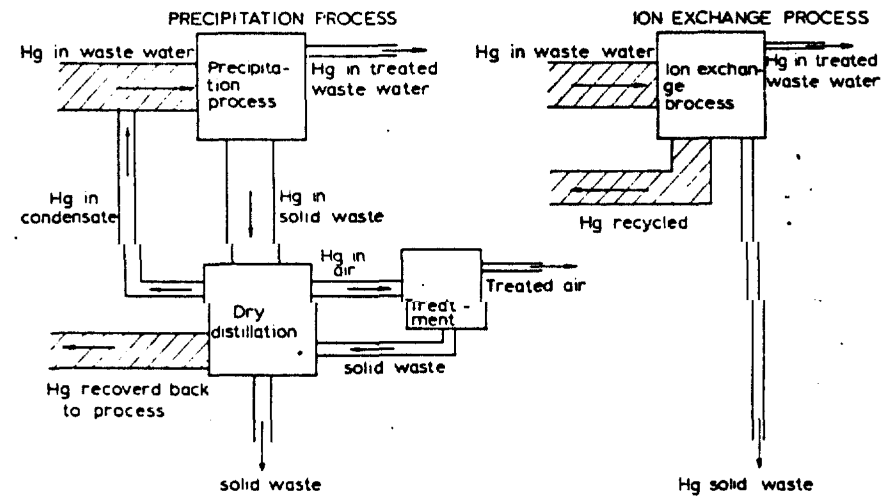

Fig. 1. Comparison of secondary problems in mercury-removing processes.

In 1970, anion-exchange resins capable of absorbing chloride-complexed mercury were available. The performance of these materials, however, was characterised by a restricted polishing power, generally resulting in a mercury level in the effluent higher than 100 ppb*, and by a low sorption capacity, due to an unfavourable sorption isotherm in the areas of low mercury and high chloride concentration. These circumstances induced Akzo to start a screening programme with more specific mercury-sorbing resins. The material selected should have a strong polishing power in order to reduce mercury in the treated effluent down to a few parts per billion, and the performance should not be seriously influenced by fluctuations in pH, temperature and the concentrations of SO_4^{2-} and ClO_3^- ions.

In order to avoid secondary waste problems, it should nevertheless be possible to regenerate the resin with a liquid that can be re-introduced into the electrolysis process. The resin should be very specific for mercury, in order to avoid introduction of impurities, which are potentially detrimental to the electrolysis process, when recycling the regenerating solution with the mercury.

Nitrogen compounds can be very dangerous in the chlor-alkali industry, as they can form the highly explosive nitrogen trichloride. Therefore, the resin should not contain nitrogen in its molecule, in order to avoid all risks of contamination.

From these screening tests, which included the study of new commercial mercury-specific resins, a new resin, originating from our own synthetic work, evolved as the best material. It was decided to develop this material in close cooperation with Akzo's sorbent-producing group Imacti** under the name Imac TMR.

IMAC TMR

Chemistry

From the literature, it is known that the mercury–sulphur bond in HgS is very

* Throughout this article the American billion (10^9) is used.

** P.O. Box 4038, Amsterdam, The Netherlands.

strong and that the solubility product of this compound is extremely low. Organic compounds that contain –SH groups are named mercaptans (derived from the Latin *mercurium captans*, seizing mercury). The Imac TMR resin developed by Akzo is a polymeric mercaptan in which thiol groups are attached to a chemically and mechanically highly inert matrix. The affinity of this thiol resin (R–SH) towards mercury proved to be very high, the strength of the resin–mercury bond being comparable to that of the mercury–sulphur bond in HgS. Thus the resin, even in saturated brine, can compete successfully with the very stable $HgCl_4^{2-}$ complex.

In brine, the following dissociation equilibria of mercury(II) chloride complexes exist:

$$Hg^{2+} + 4\,Cl^- \rightleftharpoons HgCl^+ + 3\,Cl^- \rightleftharpoons HgCl_2 + 2\,Cl^- \rightleftharpoons HgCl_3^- + Cl^- \rightleftharpoons HgCl_4^{2-}$$

Most of the mercury is then present as $HgCl_4^{2-}$ complex ions. The Imac TMR resin (R–SH) reacts preferentially with $HgCl^+$ or Hg^{2+} ions according to the reactions

$$2\,RSH + Hg^{2+} \rightarrow RSHgSR + 2\,H^+$$

and

$$RSH + HgCl^+ \rightarrow RSHgCl + H^+$$

During the reaction, the dissociation equilibria of the $HgCl_4^{2-}$ complex shift towards the $HgCl^+$ and Hg^{2+} side. Also, although these ions represent only a very small fraction of the total mercury, the affinity of the resin towards these ions is so strong that the total mercury level that remains in the liquid can be reduced to below 5 ppb, even in brine. This is illustrated by Fig. 2, which represents a breakthrough curve of an Imac TMR column on electrolysis-plant brine.

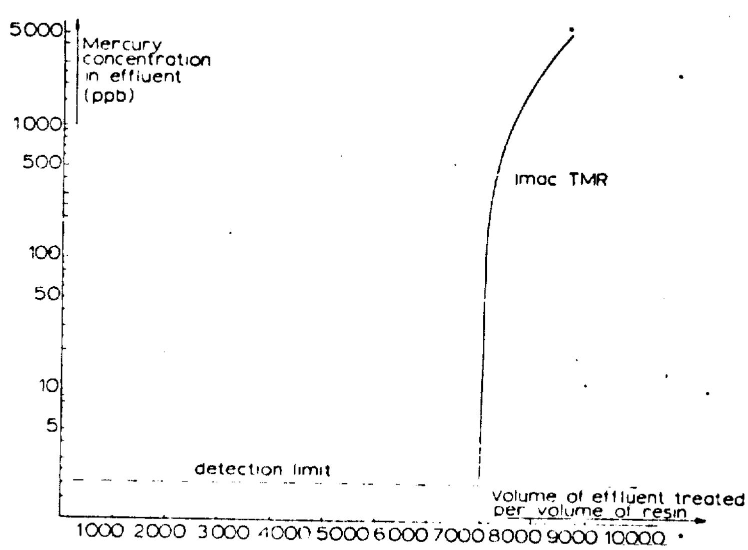

Fig. 2. Typical breakthrough curve. Chlor-alkali plant brine, pH 2. Mercury concentration in feed, 20–50 mg/l; space velocity, 10 bed volumes per hour; bed height, 1.5 m.

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being comparable to
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Capacity

The total capacity of Imac TMR is at least 1200 mequiv. of –SH per litre, which, at full loading, is equivalent to 240 g of mercury per litre of resin. The equilibrium capacity of Imac TMR depends on the concentration of mercury in the liquid phase. In Fig. 3, the equilibrium curve of Imac TMR for mercury is given, which is valid for pH values between 1 and 14 and sodium chloride concentrations between 0 and 310 g/l.

From this curve, it can be calculated that at a mercury concentration in the feed of 10 ppm, 1 m^3 of resin can treat 10,000 m^3 of waste water in one cycle. Although the amount of mercury in the resin will increase with increasing concentration in the feed, the volume of waste water per cycle will, of course, decrease. The opposite is true for lower feed concentrations.

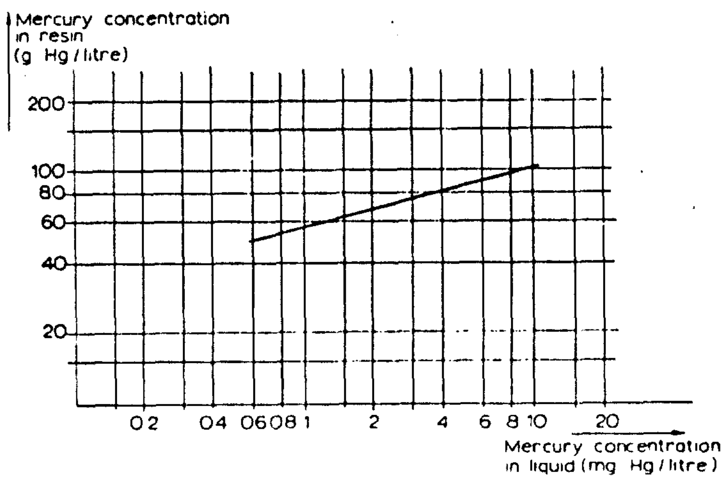

Fig. 3. Equilibrium curve for Imac TMR.

Selectivity

As mentioned earlier, the selectivity of the resin is of prime importance. Some impurities from the electrolysis process are disposed of by means of the waste water. These impurities are not necessarily detrimental for the environment. They can occur in the waste water in much higher concentrations than mercury itself and these impurities, *e.g.*, iron, can be detrimental to the electrolysis process itself. Upon regeneration of a non-selective resin, these impurities would be re-introduced into the electrolysis process. Therefore, the ion-exchange resin to be used has a prime function of retaining the mercury while all other impurities pass through.

The affinity of Imac TMR towards metal ions is related to the solubility product of the metal sulphides: the metal with the smallest solubility product of its sulphide has the highest affinity towards the resin.

A column of Imac TMR has been fed with a solution containing 10 ppm each of Hg, Cu, Pb and Cd ions, and breakthrough curves are given in Fig. 4. It can be seen that the resin initially removes all metals from the liquid. After the initial period, Cd, Pb and Cu are subsequently replaced from the resin by mercury. The concentration of the three metals in the effluent equals the concentration in the feed long before

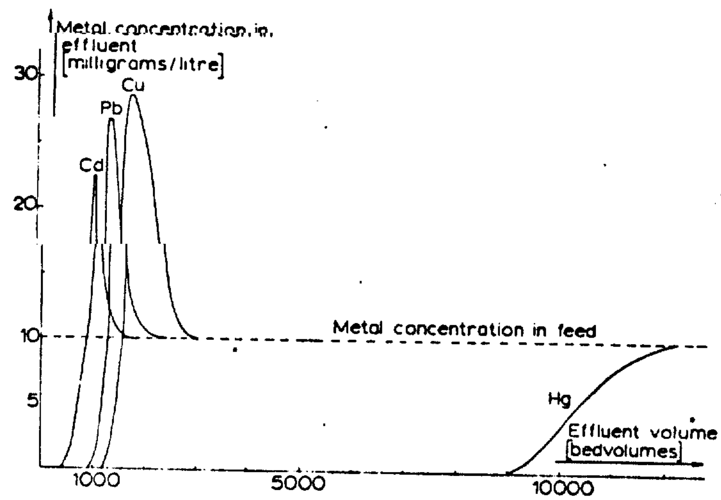

Fig. 4. Replacement of Cd, Pb and Cu ions by Hg ions when percolating a solution containing 10 ppm of each species.

mercury finally breaks through. The resin is therefore very selective for mercury in comparison with other metals.

Regeneration

Fortunately, the equilibrium of the reaction allows the resin to be regenerated with concentrated hydrochloric acid:

$$RSHgCl + HCl \rightleftharpoons RSH + HgCl_2$$

Hydrochloric acid is a common chemical in the chlor-alkali industry and is used in considerable amounts for pH adjustment of the brine circuit. The hydrochloric acid used for regeneration of the resin can serve this purpose equally well. The mercury is recycled into the electrolysis process.

THE AKZO PROCESS

In the above section, the special features of the Imac TMR were discussed. Although this resin constitutes the heart of the process, it cannot be used efficiently without appropriate pre-treatment of the waste water. This pre-treatment can determine the success of the whole operation to a large extent.

In chlor-alkali waste water, mercury can occur as metallic and as ionic mercury. This waste water can vary widely in pH and salt and chlorine content, and can contain considerable amounts of solids, including hydroxides which are difficult to filter. In some instances, the amount of waste water can fluctuate over a wide range. Coarse solids have to be removed prior to treatment, and sufficient buffer capacity has to be installed to guarantee an even flow of waste water. The Akzo Imac TMR process consists of the following stages (see Fig. 5): oxidation/pH adjustment; filtration; dechlorination; and ion exchange.

regenerated column acting as a second column for polishing the effluent of the first column.

The first unit of this process has been operating at the Akzo chlor-alkali plant in Delfzijl since May 1973. Four more plants are at the engineering stage.

Process economics

As mentioned in the Introduction, the process is not economic when based on the recovery of the mercury. A comparison of the investment and direct operating costs of this process with two alternative precipitation processes shows, however, a definite advantage over the precipitation processes (see Table I).

TABLE I

COMPARISON OF INVESTMENT AND DIRECT OPERATING COSTS OF MERCURY-REMOVING PROCESSES

Base case flow 10 m^3/h; 6 mg Hg/l; amounts in Dutch currency.

	Reduction/ filtration	*Sulphide precipitation*	*Imac TMR treatment*
Product quality	0.1–0.3 g Hg/m^3	<0.1 g Hg/m^3	< 0.005 g Hg/m^3
Investment battery limits	Dfl 570,000	Dfl 600,000	Dfl 558,000
First resin and carbon charge	–	–	Dfl 70,000
Direct operating cost in cents/m^3 water:			
Electricity	7.2	12.0	8.4
Chemicals	68.6	52.6	17.2
Resin	–	–	20.0 (5 cycles)
Carbon	–	–	6.7
Less recovered mercury at 280 $ per flask	–	–	12.6
Total	75.8	64.6	39.7
Secondary pollution problems	43 tons of solid waste, 80% moisture, with 525 kg of Hg per year	85 tons of solid waste, 80% moisture, with 525 kg of Hg per year	1 m^3 of spent resin with less than 100 g of Hg per year

Oxidation

The resin reacts only with ionic mercury, and all metallic mercury in the waste water must therefore be oxidized. For this oxidation step, chlorine or hypochlorite is used. Although the resin is not sensitive to pH, the pH of the waste water is controlled at about 3 for other reasons.

Filtration

The Imac TMR resin has a long operating cycle. In order to prevent clogging of the resin beds, good filtration is essential; either sand filters or cloth filters are used for this purpose. Hydroxides which are commonly present in chlor-alkali waste water can cause filtration problems, particularly iron hydroxide. In order to avoid these problems, the pH of the waste water is controlled at about 3 so as to keep iron in solution. As a secondary function, the filter retains mercury droplets which might pass the oxidation reactor, these droplets being oxidized in the filter.

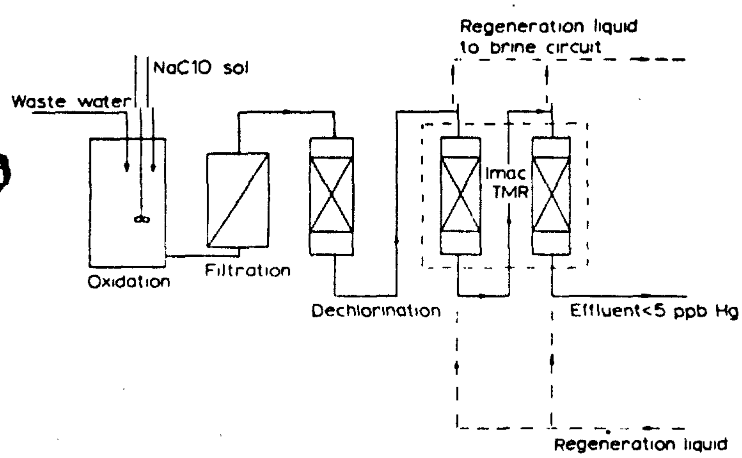

Fig. 5. Akzo Imac TMR process.

Dechlorination

The thiol groups of the resin are sensitive to oxidation and removal of the excess of oxidant is therefore necessary. In our plants, we use a column with a special activated carbon for this purpose; the column dimensions are the same as those of the ion-exchange columns.

Ion exchange

The ion-exchange columns are very similar to those used for water treatment. The flow-rate in the columns is, however, maintained at 10 volumes of waste water per volume of resin per hour. As long as a sufficient bed height of fresh resin is available, the effluent mercury concentration will be below 0.005 mg/l. There are two resin beds in series, which permits complete loading of the first resin bed in equilibrium with the influent mercury concentration. The long cycle time of the resin gives ample time to regenerate the first column before the second column starts to break through. After regeneration, the operating sequence of the columns is changed, the freshly

the AKZO IMAC TMR process for the removal of mercury from waste water

ATTACHMENT 2

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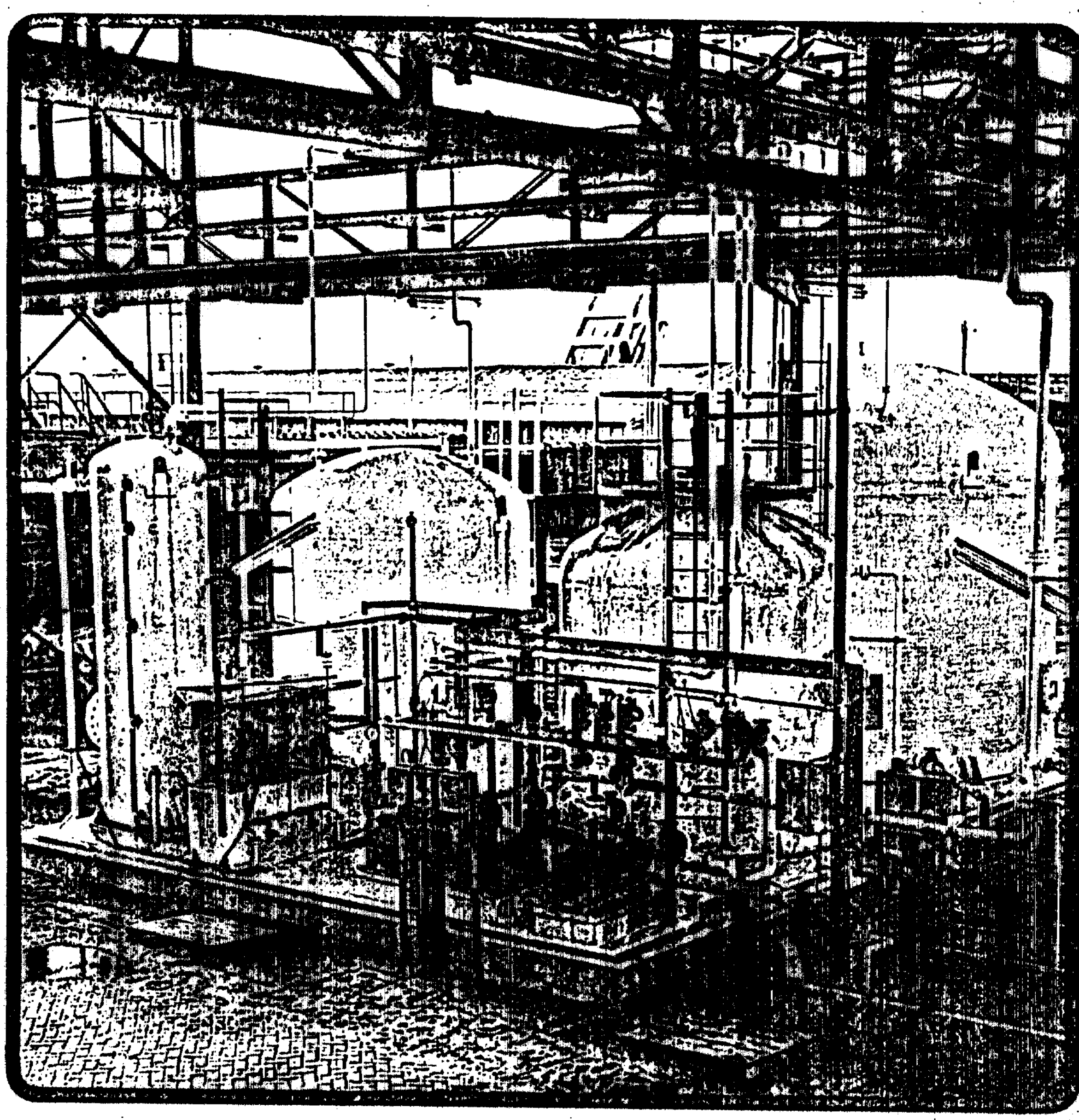
Environmental Protection
WPC—Permit



the Akzo Imac TMR process for the removal of mercury from waste water

1 Introduction

Mercury pollution is a very topical problem in view of its potential hazard to human beings.

One of the consumers of mercury is the chlor alkali industry. The majority of the mercury consumed by this industry ends up in waste streams, which are relatively well defined. Since 1970 the authorities have brought strong pressure to bear on this branch of industry to reduce mercury losses.

Previously most chlor alkali plants already operated processes for reducing mercury losses which were based on the economy of the recovery of this expensive metal. Further reduction of these losses involved the introduction of a series of additional techniques.

Today the protection of the environment against mercury pollution is the main objective of these new techniques. The value of regenerated mercury is of minor importance compared with the operational costs involved.

In recent years Akzo Zout Chemie Nederland bv (Akzo Salt Chemicals Division) has devoted considerable effort to reducing the mercury pollution arising from its own mercury-cell operated chlorine plants.
In doing so it has developed a complete mercury pollution abatement package for chlorine plants, which comprises processes for the removal of mercury from waste water, end box seal air, hydrogen and 50 % NaOH.

This brochure deals with the Akzo process for the removal of mercury from waste water.

2 The problem

When trying to solve pollution problems in which pollutants of a persistent nature are involved special care must be taken not to concentrate the pollutant in a solution or solid which cannot be recycled.

Taking this basic parameter the following criteria for the selection of a process for removing mercury from waste water can be laid down.

a Secondary pollution should be minimal.

b The mercury should be recycled.

c The residual mercury concentration in the treated effluent should be low enough to meet the most stringent regulations anticipated.

d The residual mercury concentration should not be affected by variations in the composition of the waste water, the main concern in the case of chlor alkali waste water being the NaCl concentration.

Ion exchange can in theory meet all these requirements.

In 1970 there were anion exchange resins capable of absorbing chloride-complexed mercury. The performance of these materials, however, was marked by

— a limited polishing power - resulting in a mercury level in the effluent generally higher than 100 ppb.

— a low absorption capacity - due to an unfavourable absorption isotherm in the areas of low mercury and high chloride concentration.

programme covering more specific mercury-absorbing resins. The material sought had to have:

- a strong polishing power in order to reduce mercury in the treated effluent to a few ppb's.
- its performance should not be seriously affected by fluctuations in pH, temperature and the concentrations of Cl^-, $SO_4^{=}$ and ClO_3^- ions.

In order to avoid secondary waste problems it should nevertheless be possible to regenerate the resin with a liquid which could be reintroduced into the electrolysis process. The resin should be highly specific for mercury in order to avoid introducing impurities potentially detrimental to the electrolysis process when recycling the regenerating solution with the mercury.

Nitrogen compounds can be very dangerous in the chlor alkali industry, since they can form the highly explosive nitrogen trichloride. The resin must therefore have no nitrogen compound in its molecule, in order to preclude even the smallest risk of contamination.

From these screening tests - which included the study of new commercial mercury-specific resins - a new resin was found to be the best material.
It was decided to develop this material in close cooperation with Akzo's absorbent-producing group 'Imacti' under the trade name Imac TMR.

This Imac TMR resin has been designed especially for heavy-duty performance under varying conditions in waste water.

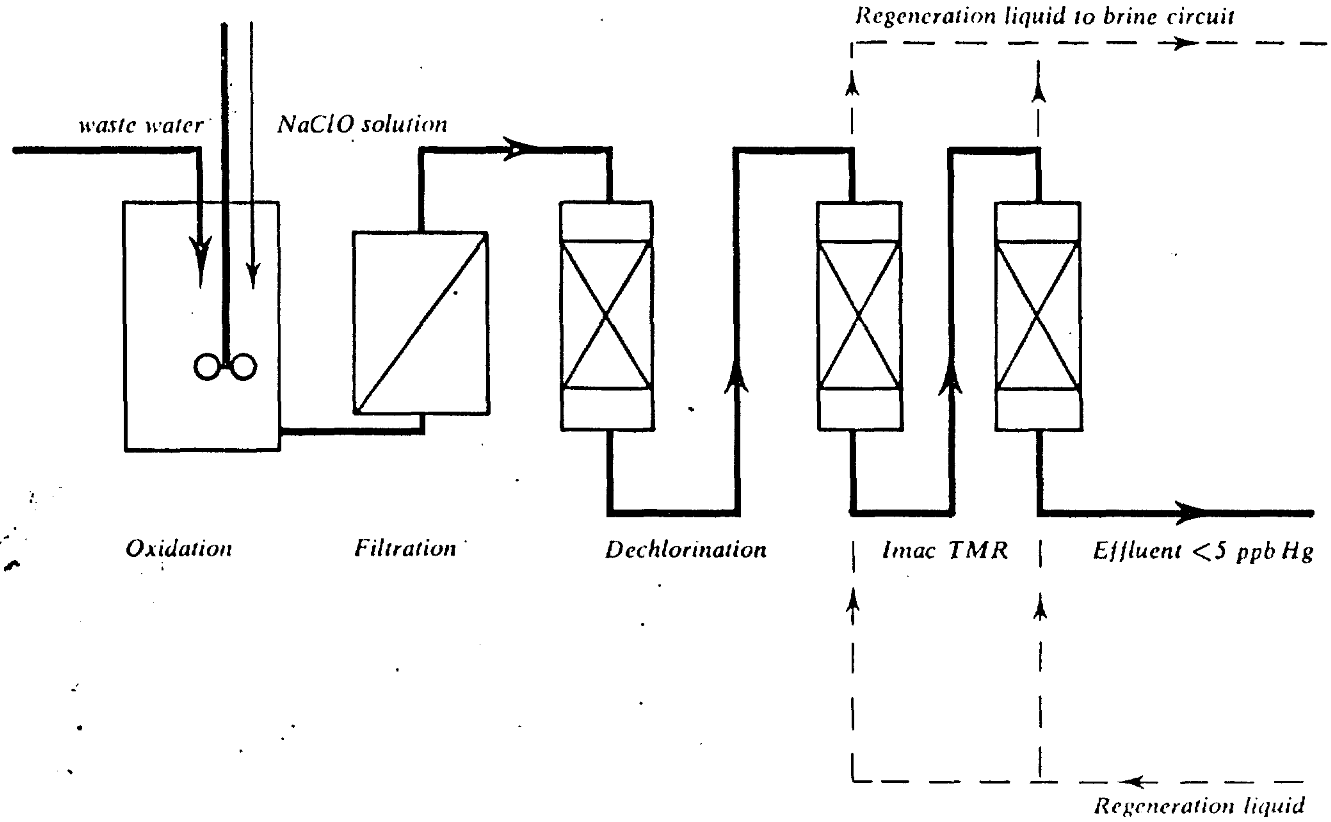
In waste water mercury can occur as metallic mercury and as ionic mercury. The waste water can vary widely in pH (in the chlor alkali industry in the salt and chlorine content as well) and can contain considerable amounts of solids, including hydroxides which are difficult to filter. In some cases the amount of waste water can fluctuate within a wide range. If coarse solids have been removed prior to treatment and sufficient buffer capacity has been installed to guarantee an even waste water flow, the Akzo Imac TMR process consists of the following stages (see Fig. 1):

- Oxidation/pH adjustment
- Filtration
- Dechlorination
- Ion exchange

Oxidation

The resin only reacts with ionic mercury. All metallic mercury in the waste water must therefore be oxidized. Chlorine or hypochlorite is used for the oxidation stage. Although the resin is not sensitive to pH, the pH of the waste water treated is maintained at around 3 for various other reasons.

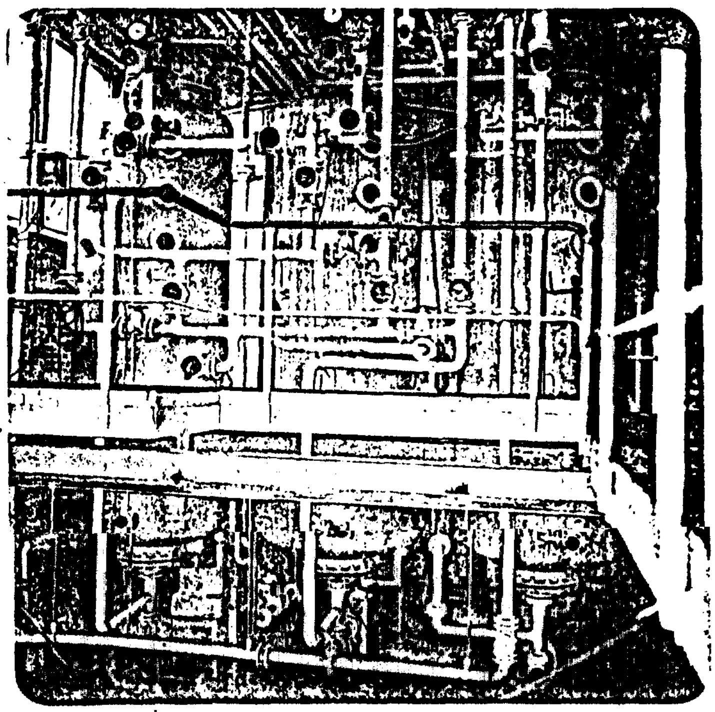
Fig. 1 Akzo Imac TMR process



The Imac TMR resin has a long operating cycle. To prevent clogging of the resin beds good filtration is essential and either sand or cloth filters are used. Hydroxides commonly present in chlor alkali waste water can cause filtration problems, particularly in the case of iron hydroxide. To circumvent these problems the pH of the waste water is maintained at around 3 to keep iron in solution.
As a secondary function the filter retains mercury droplets which might pass the oxidation reactor. In the filter these droplets have ample retention time for complete oxidation.

Dechlorination

The active groups of the resin are sensitive to oxidation and this makes removal of the oxidant surplus necessary. A column with a special activated carbon is used for dechlorination. The column has the same dimensions as the ion exchange columns.



Dechlorination and Ion Exchange columns of the Akzo Zout Chemie plant in Delfzijl, the Netherlands.

Ion exchange

The ion exchange columns are very similar to those used for water treatment. The flow rate in the columns, however, is maintained at 10 volumes of waste water/volume of resin per hour. As long as sufficient bed height of fresh resin is available, the effluent mercury concentration will be below 0.005 milligrams/litre.
There are two resin beds in series. This enables complete loading of the first resin bed in equilibrium with the influent mercury concentrations. The long cycle time of the resin is ample for regeneration of the first column before the second column starts to break through. After regeneration the operating sequence of the columns is reversed, with the freshly regenerated column acting as a second column for polishing the effuent from the first column.

4 The resin Imac TMR

Chemistry

It is known from the literature that the mercury-sulphur bond in HgS is very strong and that the solubility product of the compound is extremely low. Organic compounds having -SH groups are known as 'Mercaptans' (mercury catchers). The Imac TMR resin developed by Akzo is a polymeric mercaptan. In this resin, thiol groups (-SH) are attached to a chemically and mechanically highly inert matrix. The affinity of this thiol resin (R-SH) for mercury proved to be very high. The strength of the resin-mercury bond is comparable to that of the mercury-sulphur bond in HgS. Thus the resin, even in saturated brine, can compete successfully with the very stable $HgCl_4^{=}$complex.

The following dissociation equilibria of mercuric chloride complexes exist in brine:

$$Hg^{++} + 4Cl^- \rightleftarrows HgCl^+ + 3Cl^- \rightleftarrows HgCl_2 + 2Cl^-$$

$$HgCl_2 + 2Cl^- \rightleftarrows HgCl_3^- + Cl^- \rightleftarrows HgCl_4^{=}$$

The vast majority of the mercury is then present as $HgCl_4^{=}$complex ions.
The Imac TMR resin (R-SH) reacts preferentially with $HgCl+$ or $Hg++$ ions according to the reactions:

$$2RSH + Hg^{++} \rightarrow RSHgSR + 2H^+$$

and

$$RSH + HgCl^+ \rightarrow RSHgCl + H^+$$

During the reaction the dissociation equilibria of the $HgCl_4^{=}$ complex shift towards the $HgCl+$ and $Hg++$ side. Although these ions represent only a very small fraction of the total mercury, the affinity of the resin for these ions is so strong that the total mercury level that remains in the liquid can be reduced to below 5 ppb, even in brine. This is illustrated by Fig. 2, which shows a breakthrough curve of an Imac TMR column on electrolysis plant brine.

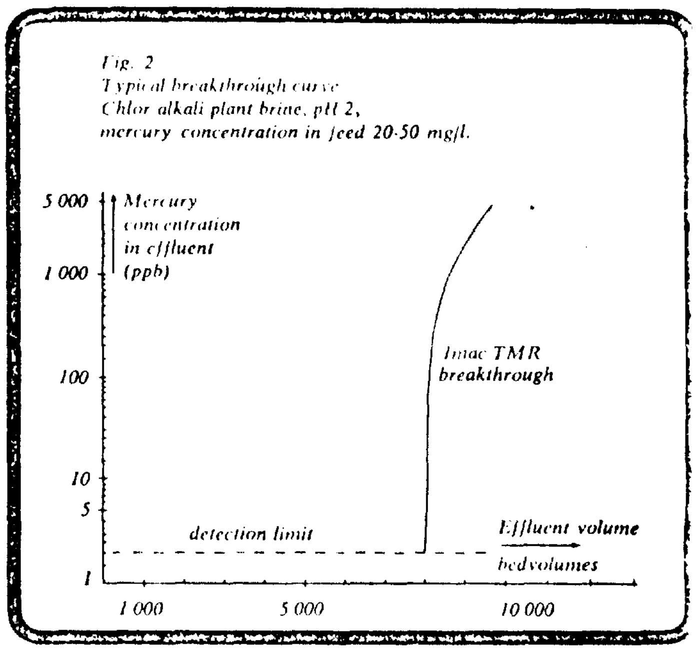
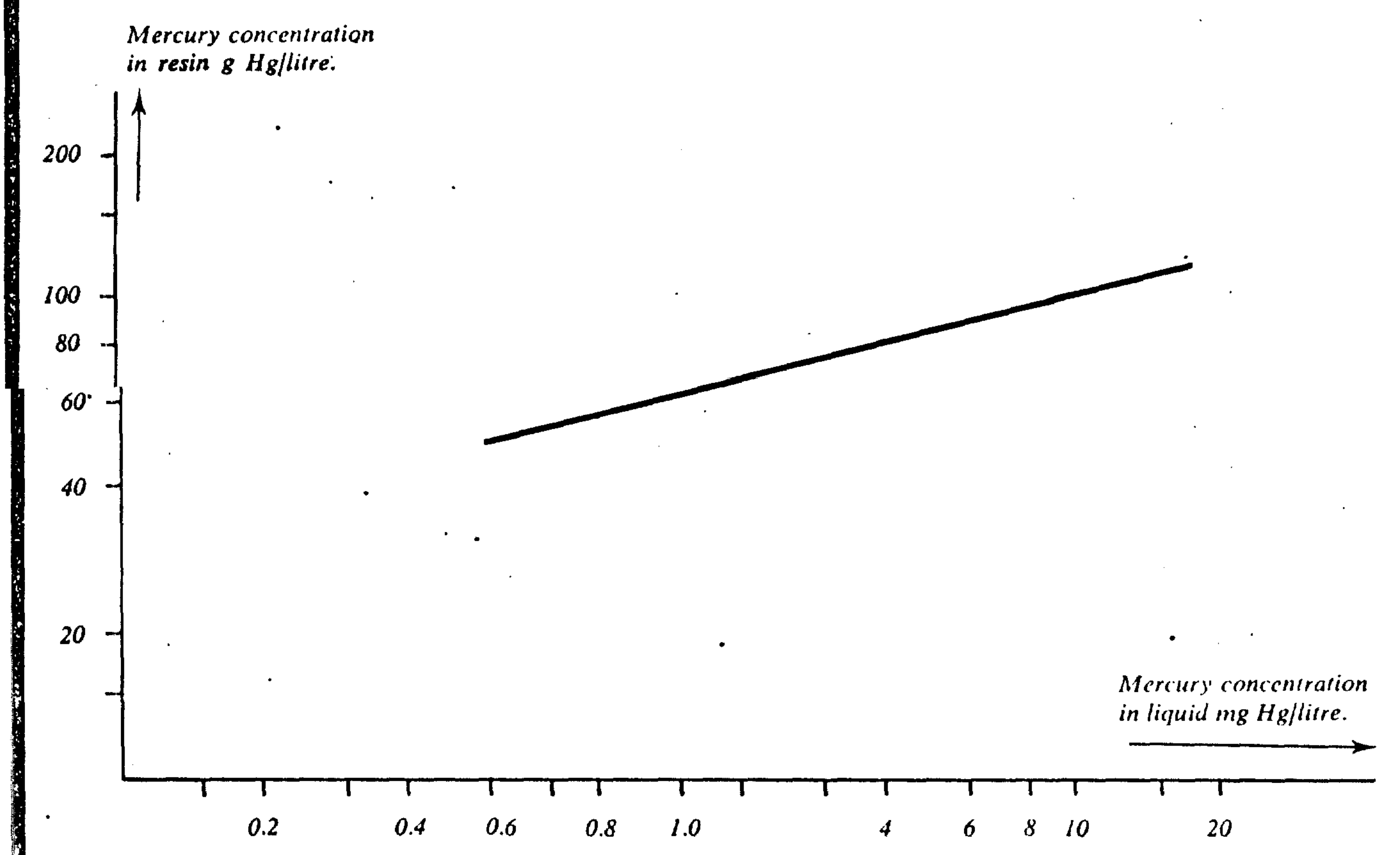


Fig. 2
Typical breakthrough curve
Chlor alkali plant brine, pH 2,
mercury concentration in feed 20-50 mg/l.

Fig. 3 Equilibrium curve of Imac TMR



Capacity

The total capacity of Imac TMR is at least 1200 milli-equivalents of - SH per litre. At full load this is equivalent to 240 grams of mercury per litre of resin. As with all ion exchange resins, the equilibrium capacity of Imac TMR depends on the concentration of mercury in the liquid phase. Fig. 3 shows the equilibrium curve of Imac TMR for mercury. This curve is valid for pH values between 1 and 14 and NaCl concentrations of between 0 and 310 grams of NaCl per litre.

From this curve it can be calculated that with a mercury concentration in the feed of 10 ppm, one cubic metre of resin can treat 10.000 cubic metres of waste water in one cycle. Although the amount of mercury in the resin will increase as the concentration in the feed increases, the volume of waste water per cycle will naturally decrease. The reverse is true for lower feed concentrations.

Selectivity

As already mentioned, the selectivity of the resin is of prime importance. The basic function of waste water is to dispose of impurities such as iron from the electrolysis process. These impurities are not necessarily detrimental for the environment. They can occur in the waste water in much higher concentrations than mercury itself, and may even be harmful to the electrolysis process.

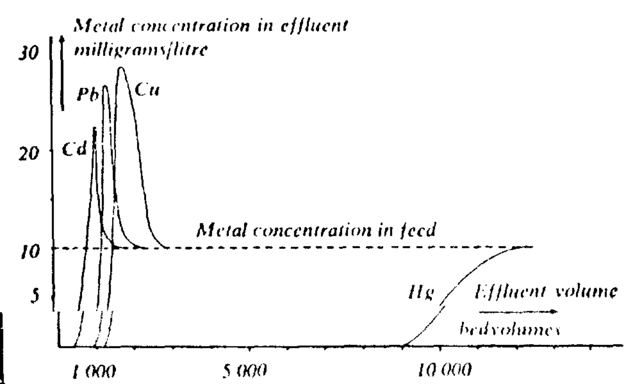
Upon regeneration of a non-selective resin these impurities would be re-introduced into the electrolysis process. The ion exchange resin to be used therefore has one main function: to retain the mercury while allowing other impurities to pass.

The affinity of Imac TMR for metal ions parallels the solubility product of the metal sulphides. The metal with the smallest solubility product of its sulphide also has the highest affinity for the resin.

A column of Imac TMR has been fed with a solution containing 10 ppm each of Hg, Cu, Pb and Cd ions. Breakthrough curves of this experiment are reproduced in Fig. 4 and

Fig. 4

Replacement of the ions of Cd, Pb and Cu by Hg ions when percolating a solution containing 10 ppm of each specimen



liquid. After the initial period Cd, Pb and Cu, in that order, are superseded in the resin by mercury. The concentration of the three metals in the effluent equals the concentration in the feed long before mercury breaks through. The resin is therefore very selective for mercury compared to other metals.

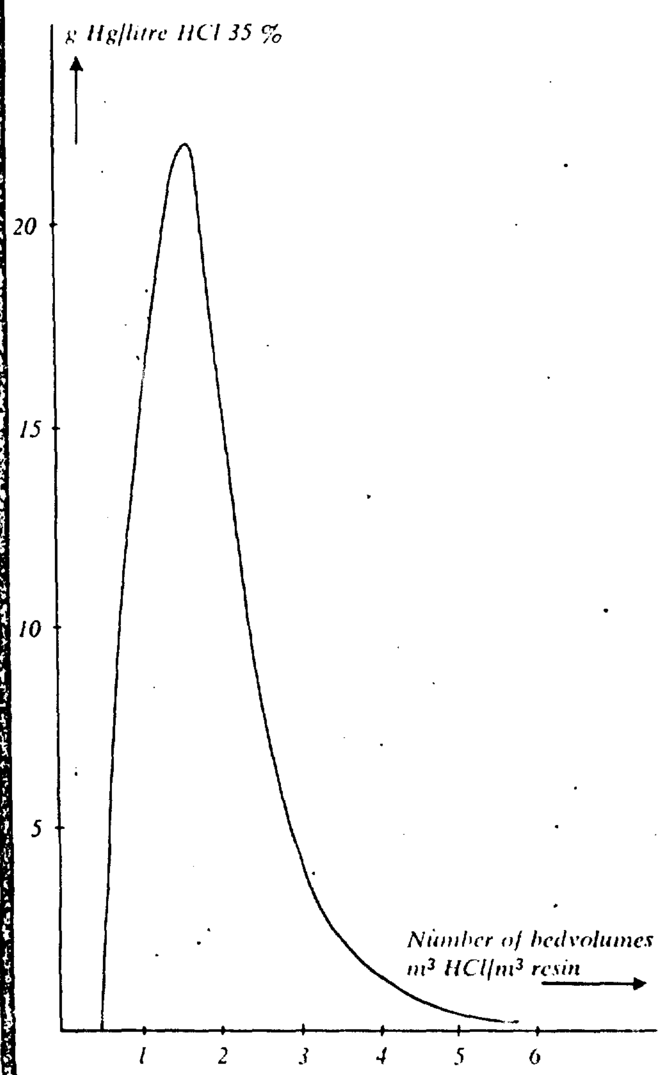
Regeneration

Fortunately the equilibrium reaction allows the resin to be regenerated with concentrated hydrochloric acid:

$$RSHgCl + HCl \rightarrow RSH + HgCl_2$$

Hydrochloric acid is a common chemical in the chlor alkali industry. It is generally used in considerable quantities for pH adjustment of the brine circuit. The hydrochloric acid used to regenerate the resin can fulfil this role equally well. The mercury is thus recycled into the electrolysis process. A typical regeneration curve is given in Fig. 5.

Fig. 5
Regeneration of Imac TMR.
with concentrated HCl. Regeneration rate
1 m³ HCl/m³ resin hour
Mercury concentration of resin
prior to regeneration 35 g Hg/litre resin



5 Process economics

As is the case with any waste water process, the investment cost required for the Akzo Imac TMR process depends to a large extent on local plant conditions. In many cases much existing equipment can be used.

Table A compares the Imac TMR process with two other processes for water treatment. This table clearly illustrates the definite advantage of the Akzo Imac TMR process over convential precipitation processes. The estimates include the installation of a buffer tank to compensate for flow fluctuations. The additional investment needed to solve the secondary pollution problems of the two precipitation processes and to recover the mercury has not been included.

Table A

	Base case flow 10 m^3/hr	at 6 mg Hg/l	Amounts in Dutch currency 1974 prices for comparison only. Exchange rate: 1 US$ approx. ƒ 2.60 = 260 cents
	Reduction/ filtration	Sulfide precipitation	Imac TMR treatment
Product quality	0.1 - 0.3 gHg m^3	< 0.1 gHg/m^3	< 0.005 gHg/m^3
Investment Battery limits	ƒ 570,000.—	ƒ 600,000.—	ƒ 558,000.—
First Resin and Carbon charge	—,—	—,—	ƒ 70,000.—
Direct operating cost in cents m^3 water			
Electricity	7.2 c m^3	12.0 c/m^3	8.4 c/m^3
Chemicals	68.6 c/m^3	52.6 c/m^3	17.2 c/m^3
Resin		—	20.0 c/m^3 (5 cycles)
Carbon	—	—	6.7 c/m^3
	75.8 c/m^3	64.6 c/m^3	52.3 c/m^3
Recovered mercury at 280 $ flask	—	—	12.6 c/m^3
Total direct operating cost	75.8 c/m^3	64.6 c/m^3	39.7 c/m^3
Secondary pollution problems	43 tons of solid waste, 80 % moisture, with 525 kg Hg per year.	85 tons of solid waste, 80 % moisture, with 525 kg Hg per year.	1 m^3 spent resin with less than 100 g Hg per year.

6 Engineering data

Flow rate (= volumes of effluent/volume of resin hour)	:	10/h
Bed depth	:	1.2 - 1.7 metres
Pressure drop, at flow rate = 10 m/h, per metre of bed depth	:	0.1 - 0.2 ata
Number of columns in series	:	preferably 2
Temperature of effluent	:	< 80°C, preferably < 40°C
pH	:	1 - 14
NaCl concentration	:	any concentration

[illegible]

The Akzo waste water treatment process for the removal of mercury from chlor alkali plant waste water is a simple single-stage ion-exchange process which guarantees a very low concentration of mercury in the effluent even under conditions of wide fluctuation.

The secondary pollution problems generated are minimal compared with other processes.

The mercury is efficiently recycled into the process.

Because of the simplicity of the process the required investment cost is relatively low, as is the direct operating cost.

The Imac TMR resin has a high capacity for mercury which is not affected by changes in pH or waste water chloride concentration. Stable operation and a low effluent mercury level can therefore be obtained under widely fluctuating conditions.

Société Nationale d'Electrolyse et de Pétrochimie (SNEP), Mohammédia, Morocco

BP Chemicals International Ltd, Sandbach, Great Britain

Borregaard Industries Ltd., Sarpsborg, Norway

Dynamit Nobel, Lülsdorf, Germany

Ciba Geigy SA, Monthey, Switserland

Kymene Oy, Kuusankoski, Finland

8 How to obtain more detailed information

The investment cost and direct operating cost of the Akzo waste water treatment process depend upon local plant conditions. To enable us to adapt the process to your requirements and to provide you with information relevant to your case, please complete the following questionnaire.

Plants in operation or under construction

Waste brine treatment.

Norsk Hydro a.s., Heröya, Norway.

Waste water treatment:

Akzo Zout Chemie, Delfzijl, the Netherlands.

Elektro-Chemie Ibbenbüren GmbH, Ibbenbüren, Germany.

Norsk Hydro a.s., Heröya, Norway.

Akzo Zout Chemie, Rotterdam, the Netherlands.

Literature (available on request)

Ir. C. J. N. Rekers — 'Some new developments in the field of mercury pollution abatement by Akzo'. Proceedings of The Chlorine Institute's Plant Managers' Seminar. Houston February 7, 1973. Page 14-1.

Dr. G. J. de Jong, Ir. C. J. N. Rekers — 'The Akzo process for the removal of mercury from waste water'. Proceedings of the First World Mercury Congress. Barcelona May 1974. Volume 1, page 377.

also published in: Journal of Chromatography Volume 102 (1974) page 443-451.

Photography: E. de Boer

Please send to:
Akzo Zout Chemie Nederland bv
Licensing Department
P.O. Box 25
Phone (05400) 53241
Telex 44312
Hengelo (O.), Holland

Name of company

Location address

Person to contact

Plant capacity

Type of cells

Waste water flow

How is water treated at present?

Mercury content of untreated waste water

Mercury content of treated waste water

Mercury level to be obtained

pH of water to be treated

Free chlorine content

Average salt content

Other chemicals, sulphite, sulphide, chlorate, sulphate present in waste water stream

Solids content of water to be treated

What level of engineering does your company prefer for a waste water treatment plant?

- Process engineering only ☐
- Detailed engineering ☐
- Turn-key project ☐
- To be discussed ☐

Akzo

is a company, based in the Netherlands, worldwide engaged in the development, the production and the marketing of chemicals, fibers, pharmaceutical products, coatings and a variety of consumer products.
In 1976 sales were over four billion dollars and employment world wide over 92.000.

Akzo Zout Chemie Nederland bv

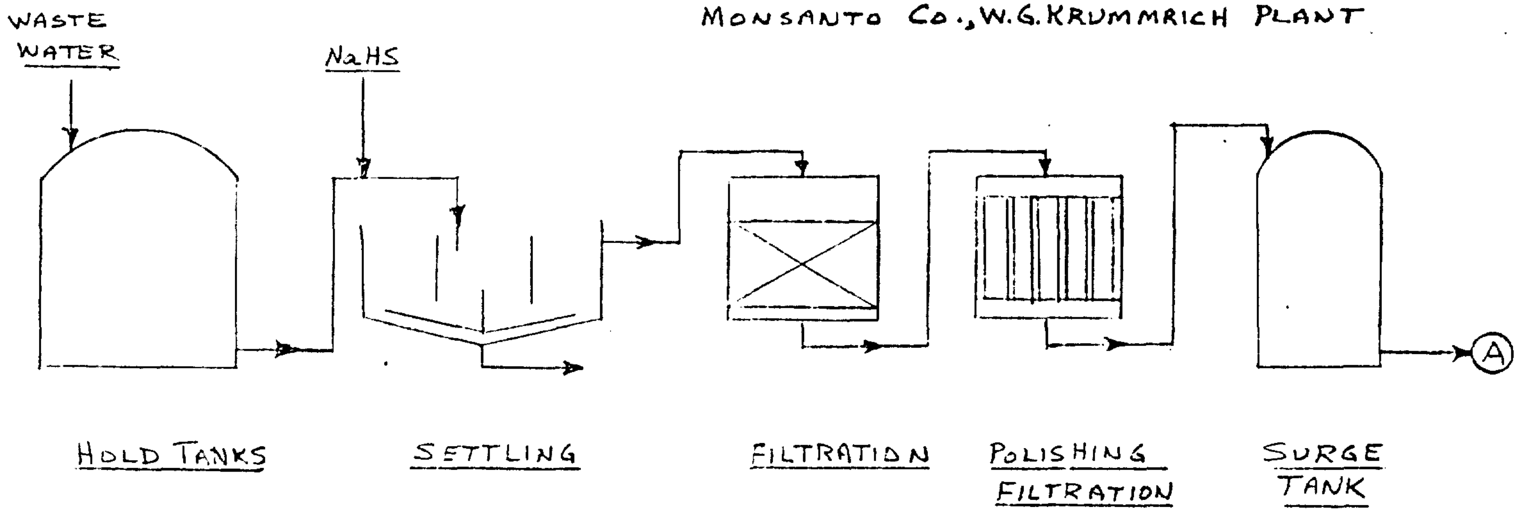
is the bulk chemicals division of Akzo, largest evaporated salt producer in the world, (more than 4,000,000 tons annual capacity), and involved in chlorine, caustic, soda ash, vinyl-chloride and methanol activities on a big scale.

AKZO

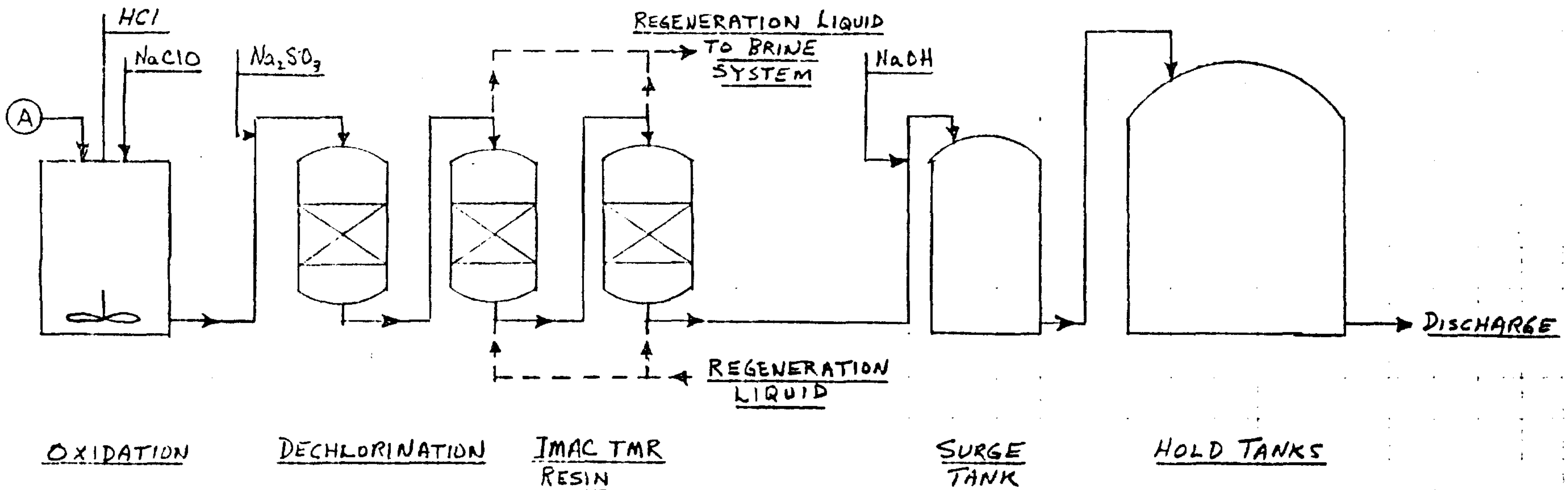
ATTACHMENT 3

WASTE WATER DEMERCURIZATION PROCESS

MONSANTO CO., W.G. KRUMMRICH PLANT



EXISTING SULFIDE TREATMENT

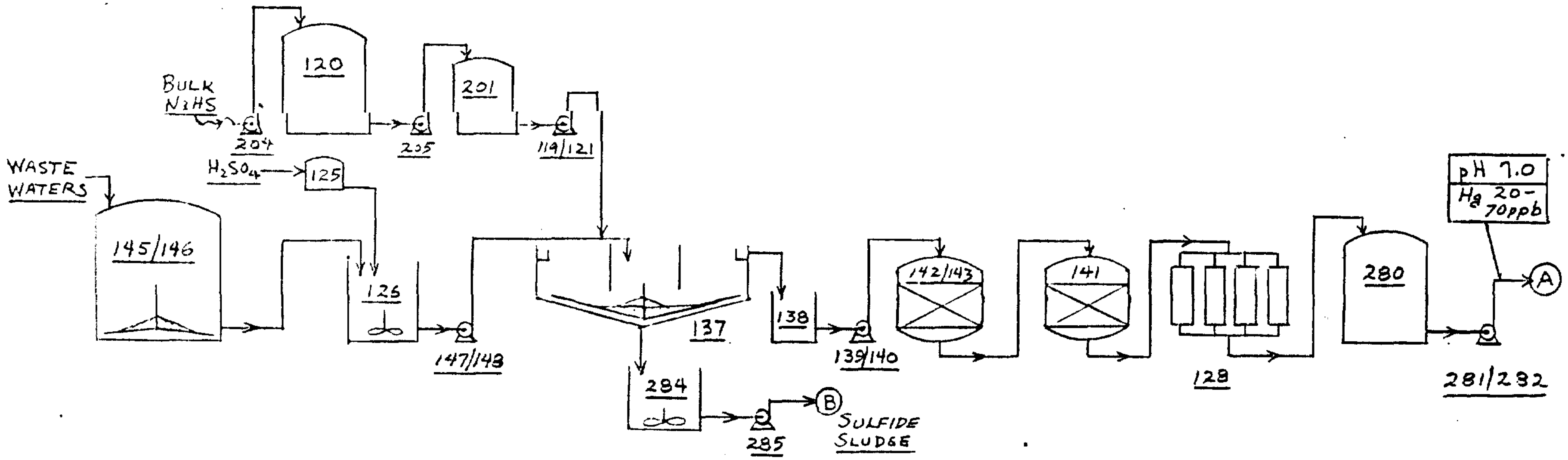


NEW AKZO IMAC TMR TREATMENT

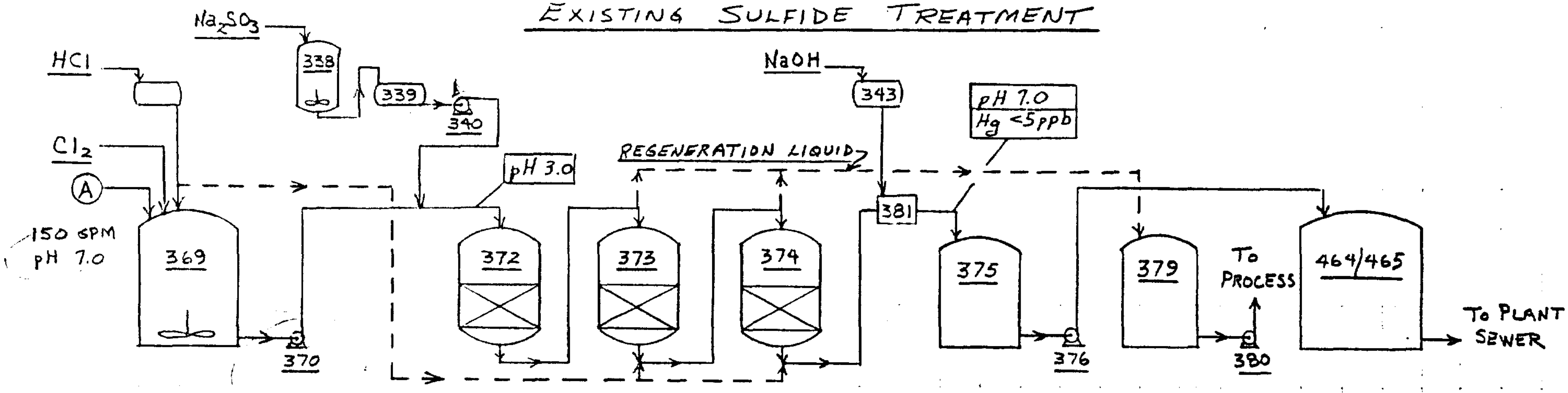
ATTACHMENT 4

WASTE WATER DEMERCURIZATION PROCESS

MONSANTO CO. W.G. KRUMMRICH PLANT



EXISTING SULFIDE TREATMENT



NEW AKZO IMAC TMR TREATMENT

Existing Sulfide Treatment

ATTACHMENT 5
page 1 of 2

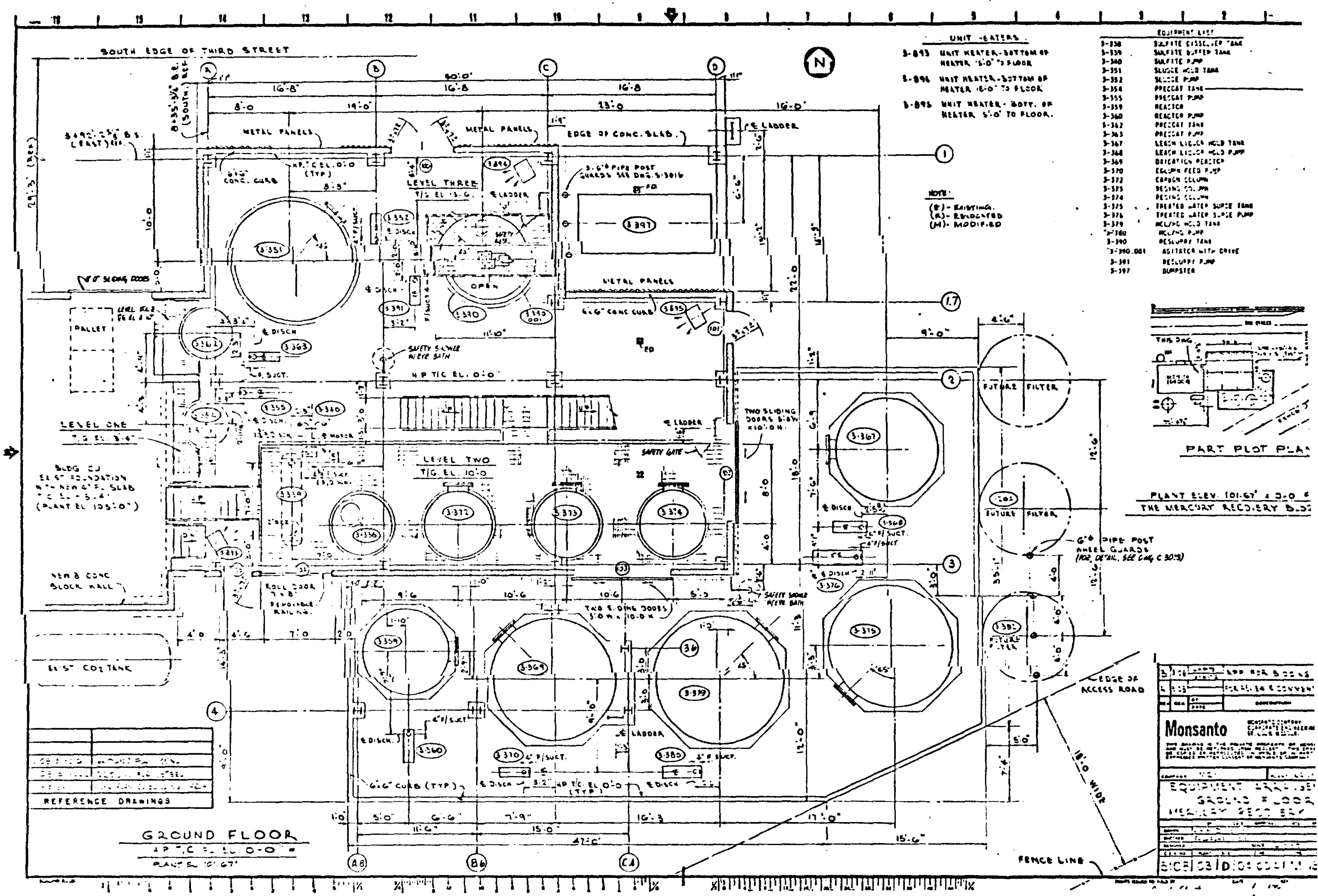
Item No.	Name / Description
119/121	Sulfide Feed Pumps
120	NaHS Storage Tank (3,700 gals.)
125	Sulfuric Acid Head Tank (200 gals.)
126	Acid Mix Tank (1,000 gals.)
128	Polishing Filter
137	Sulfide Clarifier (35'ϕ x 14' high)
138	Sulfide Clarifier Surge Tank (1,270 gals.)
139/140	Sulfide Filter Feed Pumps
141	Activated Carbon Filters (10'ϕ x 4' Infilco)
142/143	Coal Filters (9'ϕ x 4' Infilco)
145/146	Waste Water Surge Tanks (400,000 gals)
147/148	Waste Water Surge Tank Pumps
201	Sulfide Mix Tank (500 gallons)
204	NaHS Unloading Pump
205	NaHS Transfer Pump
280	Surge Tank (20,000 gals.)
281/282	Surge Tank Pumps
284	Sulfide Sludge Tank (1,500 gals.)
285	Sulfide Sludge Tank Pump

Equipment in Use

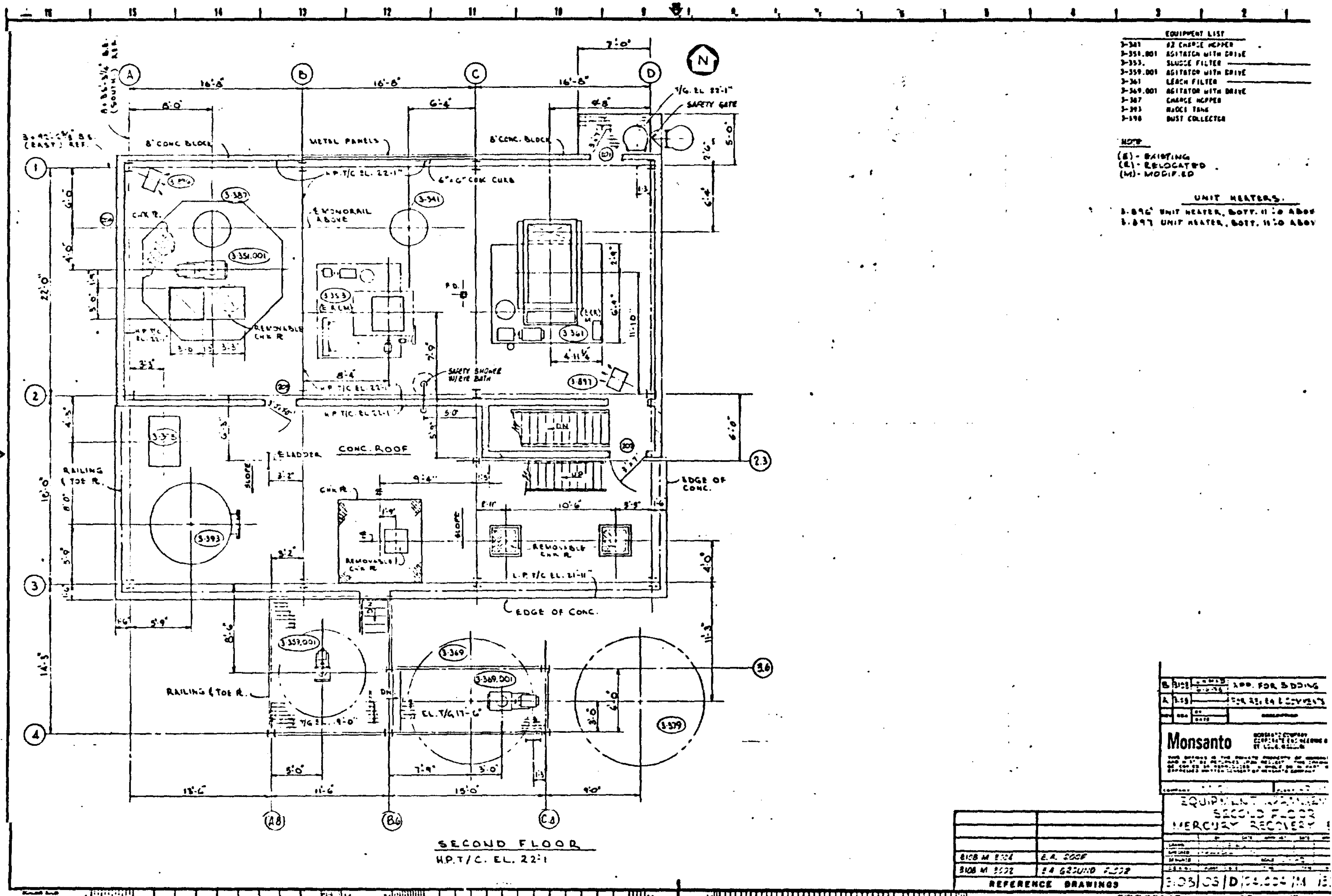
New AKZO Imac TMR Treatment

ATTACHMENT 5

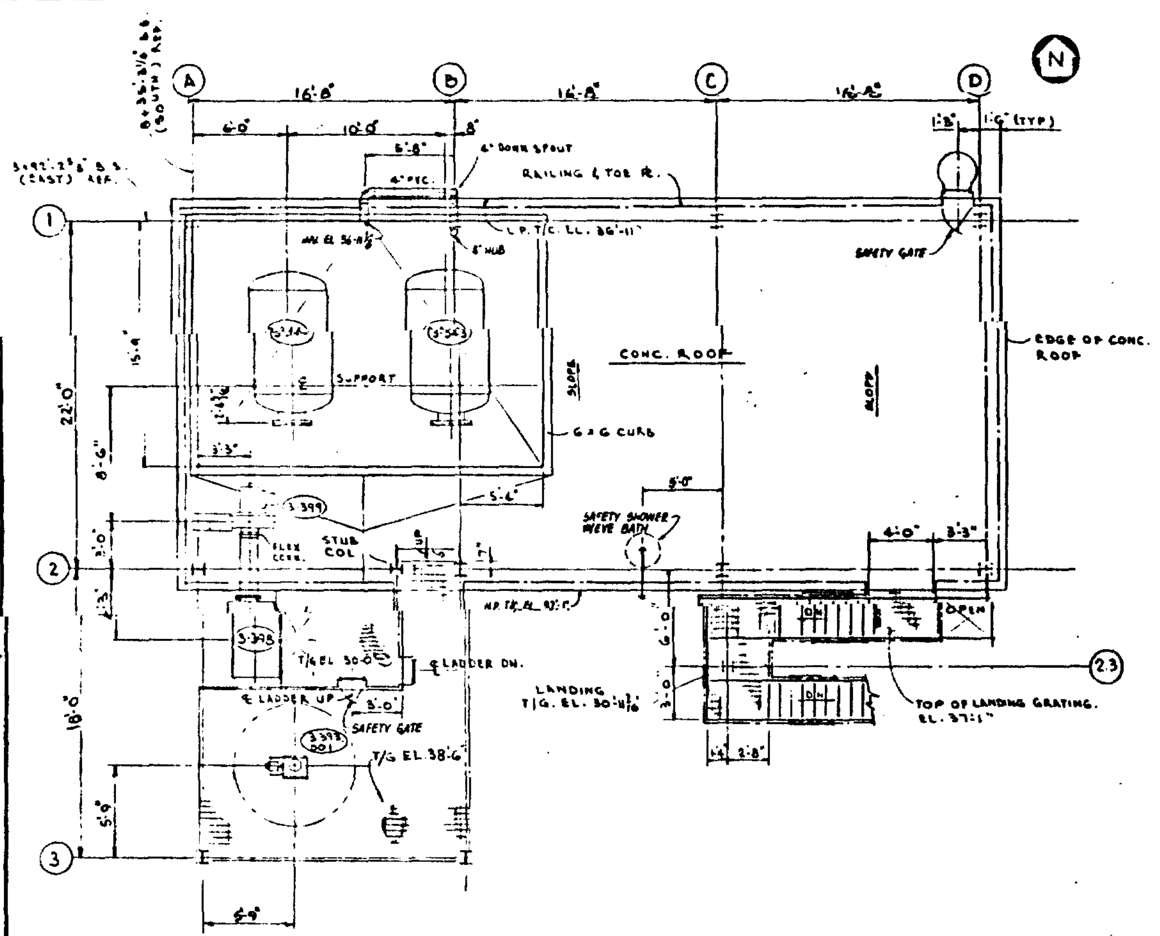
Item no.	Name / Description
338	Sulfite Dissolver (1440 gals.)
339	Sulfite Buffer Tank (180 gals.)
340	Sulfite Pump
343	NaOH Head Tank (1000 gals.)
344	HCl Head Tank (1000 gals.)
369	Oxidation Reactor (11,000 gals.)
370	Column Feed Pump
372	Carbon Column (3,000 gals.) (165 cu. ft. activated carbon packing)
373/374	Resin Columns (3,000 gals. each) (each w/165 cu. ft. IMAC TMR Resin)
375	Treated Water Surge Tank (17,000 gals.)
376	Treated Water Tank Pump
379	HCl/Hg Hold Tank (13,600 gals.)
380	HCl/Hg Pump
381	In-Line Mixer
464/465	Waste Water Hold Tanks (400,000 gals. each)



ATTACHMENT 6



ATTACHMENT 7



ROOF
H.P. T/C. EL. 37'-1"
L.P. T/C. EL. 36'-11"

EQUIPMENT LIST

3-343	NaOH HEAD TANK
3-344	HCL. HEAD TANK
3-393.001	AGITATOR WITH DRIVE
3-399	FAN

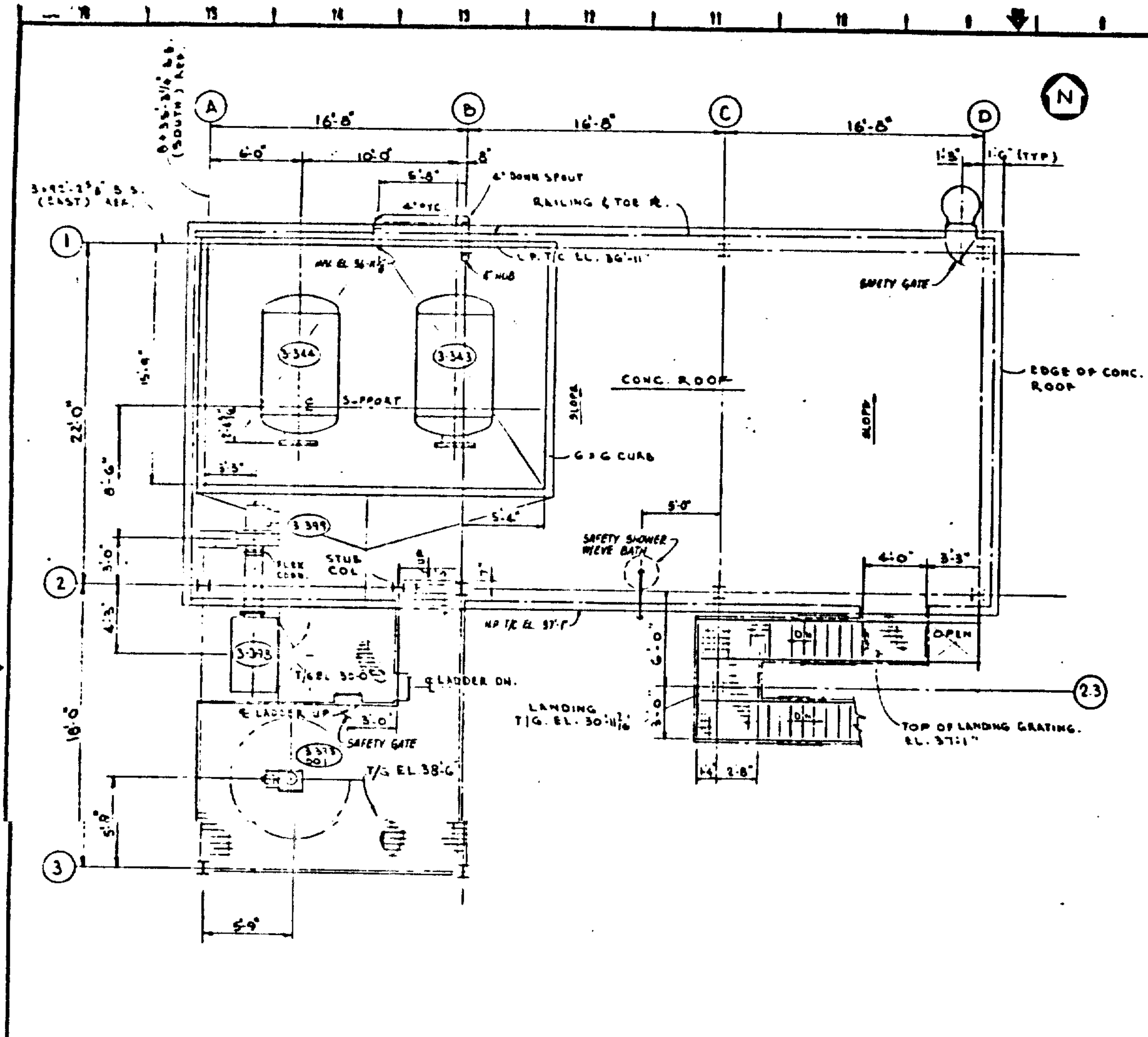
3108 M 2003	E.A SECOND FLOOR
3106 M 2002	E.A SECOND FLOOR
REFERENCE DRAWINGS	

APP. FOR BIDDING
FOR REVIEW & COMMENT

Monsanto

EQUIPMENT ARRANGEMENT
ROOF
MERCURY RECOVERY

ATTACHMENT 8



ROOF
H.P. T/C. EL. 37'-1"
L.P. T/C. EL. 36'-11"

EQUIPMENT LIST

3-343	NaOH HEAD TANK
3-344	HCL. HEAD TANK
3-393.001	AGITATOR WITH DRIVE
3-399	FAN

3108 M 3003	E.A. SECOND FLOOR
3108 M 3002	E.A. GROUND FLOOR
REFERENCE DRAWINGS	

Monsanto

EQUIPMENT ARRANGEMENT
ROOF
MERCURY RECOVERY

3.08 C3 D

ATTACHMENT 8

quate and complete waste treatment along the Mississippi River has been frustratingly slow. However, attention is directed to the fact that every Corps. Levee Pump Station serving a municipality along the river pumps raw or partially treated sewage to the river during high stages. The Corps must bear with us a while longer, until proper secondary type treatment works are completed.

Very truly yours,

C. W. Klassen
Technical Secretary

CWK:cj

cc: -Collinsville Office
-H. W. Foster
-Village Clerk

bc: -Carl Klein
-Mike Purlee
-Rep. Price

6. Sauget was attempting to operate the active fill area on a slope with compaction although there was one over at the end of the fill approximately 40-foot wide with refuse 4 to 5 feet deep where compaction was not satisfactory.

7. A small pool of surface water (approximately 30' X 40') due to recent rainfall was observed at the end of their current operation. This was pointed out to Mr. Sauget and he was advised that if this condition should continue to exist, it would be necessary for him to either divert the surface water or provide portable pumping facilities for removal.

R. L. Schleuger
Regional Sanitary Engineer

RLS:skv

cc: Region VI